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Near-infrared surface plasmon resonance sensing on a Si platform with nanoparticle-based signal enhancement

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Abstract

A Si-based surface plasmon resonance (SPR) system is examined in conditions of the nanoparticle-enhanced sensing. The system is equipped with near IR pumping light and a silicon coupling prism, used with SPR-supporting gold film in the Kretschmann–Raether geometry. Using Maxwell–Garnett (MG) effective medium theory, we modeled the SPR-related response of the system to the absorption of colloidal nanoparticles of different materials (Au, Cu, Pt, Ag, Al, Ti, Pd) on gold. We show that this response strongly depends on the nanoparticle fill factor, associated with a relative volume of nanoparticles in the absorbed layer. For low fill factors ($f_m \sim 0.1$), corresponding to relatively low concentrations of small nanoparticles, the absorption of nanoparticles of different materials leads to almost identical angular shifts of the SPR dip, but to a quite different intensity damping at the dip point. In contrast, the increase of the fill factor results in quite different angular and intensity SPR characteristics for the materials used, with the most pronounced sensing responses for Pt, Pd and Ti. The proposed analysis enables to estimate the efficiency of nanoparticles of different materials as markers in nanoparticle-enhanced SPR sensing.

Keywords: Surface plasmon resonance; Absorption sensing; Nanoparticle-enhanced sensing

1. Introduction

With an impressive progress of biosensing methods over the last decade, surface plasmon resonance (SPR) has emerged as a leading technology for a real-time, label-free detection of biological binding and recognition events [1]. SPR is observed as a dip of reflectivity of light, directed through a glass (dielectric) prism and reflected from a thin (generally, 40–50 nm) gold film, deposited on it, at a specific combination of wavelength and intensity [2]. The conventional SPR transduction principle is based on a resonant dependence of parameters of light, reflected from the gold, on the refractive index of an adjacent thin layer [3]. A reactant is usually immobilized on gold and then brought into contact with its analyte partner present in a solution. Changes of the biolayer thickness due to the binding interaction, accompanied by a refractive index change, lead to a change of SPR conditions, which can be followed by angular [3–5], wavelength [6,7], or phase [8,9] characteristics of light.

However, the conventional SPR transduction principle becomes less efficient when changes of refractive index are extremely small, as e.g., in cases of protein complexation or the adsorption of ultra-small biological agents such as low-molecular weight drugs. To enhance the sensing response in such situations, it has been proposed to use colloidal Au nanoparticles as markers of objects of interest [10]. The adsorption of even a small quantity of an absorbent material on the gold surface leads to an effective plasmon wave damping and consequently to a decrease of the reflected intensity at the

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resonance point. This enables to improve the resulting sensor sensitivity. By now, only gold nanoparticles have been intensively tested in such a regime of SPR sensing [10,11], while information on sensing properties of nanoparticles of other materials is essentially absent. Nevertheless, nanoparticles of other metals could be even more efficient in the configuration of nanoparticle-enhanced sensing.

This paper is devoted to a comparative analysis of SPR sensor responses when nanoparticles of different metals are used as markers in the nanoparticle-enhanced SPR sensing. All studies were performed in the configuration of the Si-based SPR coupling, which we recently introduced with the anticipation to extend the operation of SPR sensors to IR range and miniaturize them, taking advantage of much better state of development of Si-based microfabrication technologies compared to the glass ones [12–15].

2. Results and discussion

In this study, we consider the Kretschmann–Raether arrangement [2] with the use of a Si-based coupling technology [12–15]. In this technology, a Si prism is used instead of the glass one, as shown schematically in Fig. 1. The system also includes a thin (40-nm) gold film on the prism. The nanoparticle-enhanced sensing is modeled by the deposition of a thin absorbent layer (the absorbance implies the presence of a metallic material with non-zero imaginary part), consisting of identical nanoparticles of different metals (Au, Cu, Pt, Ag, Al, Ti, Pd). We imply that this layer contains a monolayer of metal nanoparticles, as shown in Fig. 1. Therefore, the thickness of this layer is equal to the size of nanoparticles. Such a layer can be characterized by the fill factor f_m, which is associated with the volume, occupied by the nanoparticles relatively to the total layer volume ($f_m = 1$ corresponds to the extreme case of the continuous film, when the nanoparticles fill the whole volume of the layer).

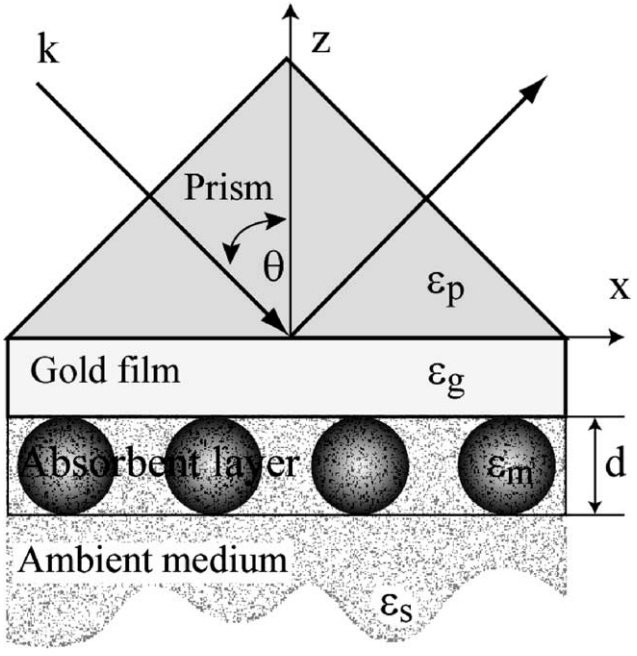

Fig. 1. Schematic of used Kretschmann–Raether prism arrangement with an absorbent nanoparticle-based layer.

Conditions and parameters of plasmon excitation have been determined by Fresnel's formulas using the matrix method [16]. Dielectric constants of the metals used were taken from the SOPRA database of refractive indices [17]. The effective dielectric constant of the absorbent layer was obtained from Maxwell–Garnett (MG) effective medium theory, also known as the Clausius Mosotti relation [18]. This theory considers a two component medium, in which small inclusion particles (e.g., nanospheres) are embedded in a homogeneous host medium with different dielectric property. The theory uses the conclusion of classical theories of inhomogeneous media that the material can be treated as an homogeneous substance with an effective dielectric function and an effective magnetic permeability, if the electromagnetic radiation wavelength is much larger than the particle size [19]. In our conditions of near-IR light, this is essentially the case for sizes of nanoparticles up to 100–200 nm. It should be also noted that the theory gives relatively precise results only for relatively low fill factors ($f_m = 0.1$–0.2). This limitation is caused by the contribution of dipole interactions, which start to play an important role at relatively high concentrations of nanoparticles. Nevertheless, for all basic dependences the correction coefficient due to dipole interactions is known to be insignificant up to fill factors of $f_m = 0.5$ [20]. According to the MG theory, the dielectric constant can be derived as follows:

$$\varepsilon_{\text{eff}} = \varepsilon_s \left(\frac{\varepsilon_m(1 + 2f_m) + 2\varepsilon_s(1 - f_m)}{\varepsilon_m(1 - f_m) + \varepsilon_s(2 + f_m)} \right), \quad (1)$$

where ε_m, ε_s are dielectric constants of the nanoparticles and of the ambient medium, respectively.

In our calculations, we considered two different values of fill factors, which correspond to qualitatively different situations. The first one ($f_m = 0.1$) describes the case of a relatively large distance between nanoparticles (the mean distance between particle equal 2.5 particle diameter). The second value ($f_m = 0.5$) corresponds to a maximal possible fill factor, when the particles are closely packed [10].

To verify the validity of performed calculations, we also carried out control tests in the Kretschmann–Raether arrangement. The gold film (40 nm) was deposited on a Si prism (p-type, $\rho > 20\,\Omega$cm, Almaz Optics, West Berlin, NJ) with a base angle of $\alpha = 16.6°$, custom made for our study. Such prism conditioned the inci-

dence of the laser beam onto the silicon/gold interface at angles close to θ_{SPR} obtained from theoretical calculations. A nanoparticle-based continuous layer of some materials (Cu, Ti, Al) was deposited on the gold film by a method of pulsed laser ablation [21]. In brief, in this method UV laser radiation is used to ablate a metal target and thus naturally produce metal nanoparticles, which then are deposited on a substrate in a residual inert gas (He), forming a thin nanoparticle film. The method makes possible fine variations of nanoparticle size by a change of ablation parameters (details on the laser ablation method can be found in [21]). In the first approximation, such a nanoparticle-based film corresponds to the extreme case of the highest fill factor ($f_s \sim 0.5$) [10,11]. The SPR coupling system (with or without the flow cell) was placed onto a rotary block of a variable angle spectroscopic ellipsometer (Woollam VASE® ellipsometer, J.A. Woollam, Lincoln, NE) to allow for a very fine variation of the angular prism position with respect to the optical path of the ellipsometer, while the reflected intensity was recorded by a photodetector.

SPR response analysis can be carried out in configurations of both the angular interrogation, when the SPR dip-related angle position is recorded under the fixed wavelength, and the intensity interrogation, when the reflected intensity near the SPR dip is monitored under the fixed angle and wavelength. Fig. 2 presents the angular position of the SPR dip (a) and the reflected intensity at the SPR dip (b) as a function of the absorbent layer thickness for a relatively low fill factor of $f_m = 0.1$. One can see that the thickness increase, corresponding to the increase of the nanoparticle size, leads to the shift of the SPR angle to higher values and a change of the reflected intensity. However, the angular shift is almost identical for nanoparticles of different materials, suggesting that metals, different from gold, can give similar responses in the nanoparticle-enhanced sensing. Furthermore, the responses of other nanometals appear to be more significant in the case of the intensity interrogation, as shown in Fig. 2b. Indeed, this figure suggests that the system is much more sensitive with Pt and Ti nanoparticles, compared to Au and Ag ones, mainly used in surface plasmon resonance-based schemes. The difference of results for angular and intensity interrogations can be explained by the fact that the shift of the resonant angle is related to the change of the medium refraction, connected to the real part of the dielectric function, whereas the reflected intensity is related to the medium absorption, associated with its imaginary part. We reason that the use of nanoparticles of different metals changes first of all the light absorption, since imaginary parts of the dielectric function are known to be essentially different for different metals. In particular, for Ti, Pt and Pd with the largest imaginary parts the intensity responses appear to be maximum.

Fig. 3 shows the angular position of the SPR dip (a) and the reflected intensity at the SPR dip (b) as functions of the fill factor of a 20 nm-thick absorbent layer, deposited on the gold surface. One can see that the sensing response is proportional to the value of fill factor. Here, different metal inclusions cause almost similar shifts of the resonant angle (Fig. 3a) and quite different damping of the intensity at the SPR minimum (Fig. 3b). As shown in Fig. 3b, materials with a relatively large imaginary part (Pd, Pt and especially Ti) demonstrate the strongest response to the nanoparticle-enhanced sensing at relatively high f_m, while Au and Ag show a relatively weak reaction. In particular, for highest fill factors ($f_m \sim 0.5$), corresponding to a complete coverage of the gold film, we have the change of reflected intensity by 25% for Ti and 8% for Pd. Comparing these values from the calculations with ones obtained from the experiment (19% and 7% for Ti and Pd, respectively), we can conclude that the proposed model gives a satisfactory description of the nanoparticle-enhanced sensing.

Note that the results for relatively high fill factors approach the ones for the case of the continuous film, which is a typical configuration of the absorption sensing [11,22]. We recently showed [23] that the responses of the SPR system in the absorption sensing regime

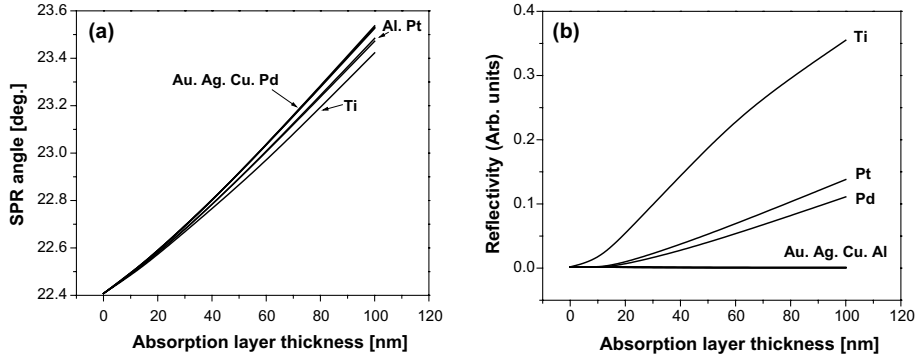

Fig. 2. Calculated SPR angular shift (a) and reflected intensity at a minimum of SPR curve R_{min} (b) as a function of the thickness of the absorbent layer. The data are given for $\lambda = 1200$ nm with different nanometal inclusions for $f_m = 0.1$. The curves are calculated for an aqueous ambient medium ($n = 1.33$).

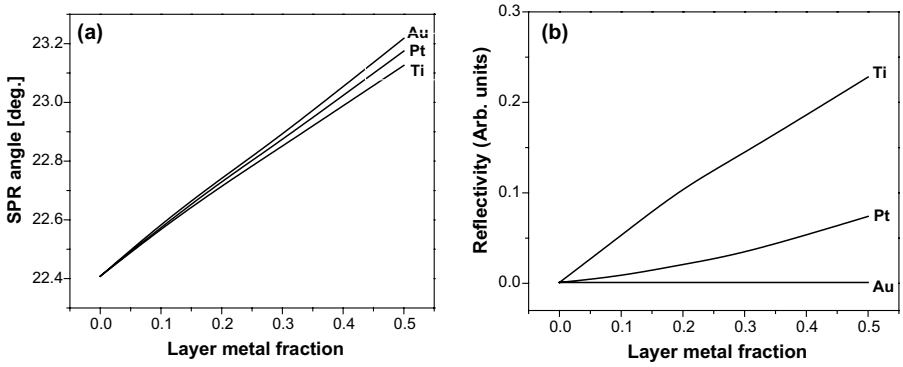

Fig. 3. Calculated angular shift (a) and the intensity change (b) as a function of the metal layer fill factor f_m for a 20-nm nanocomposite layer of different materials. The data are given for the pumping wavelength of $\lambda = 1200$ nm and the aqueous ambient medium.

are quite different for different metals (Al, Au, Ag) and semiconductors (Si).

3. Conclusions

Thus, we established the behavior of near-IR light reflectivity characteristics in a silicon- based configurations, using absorbent layers of different metal nanoparticles. The approach used is also well suited for the characterization of the absorbent layers of metals. We reason that for the precise solution of equations of this sensor type one have to take into consideration effects related both to the presence of the underlying plasmon supporting film and to interparticle interactions.These effects can be taken into account through the particle-surface coupling [24] and particle-particle interaction at the superficial layer fraction [25].These studies are in progress and will be published elsewhere.

The presented results explain the potential of using nanoparticles of different metals in nanoparticle-enhanced SPR sensing. The variety nanoparticles, available on the market, offers such an attractive opportunity.

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